

Gaussian to Exponential Crossover in the Attenuation of Polarization Echoes in NMR

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An ingenious pulse sequence devised by S. Zhang, B. H. Meier, and R. R. Ernst (Phys. Rev. Lett. **69**, 2149 (1992)) reverses the time evolution (“spin diffusion”) of the local polarization in a dipolar coupled ¹H spin system. This refocusing originates a Polarization Echo whose amplitude attenuates by increasing the time t_R elapsed until the dynamics is reversed. Different functional attenuations are found for a set of dipolar coupled systems: ferrocene, $(C_5H_5)_2Fe$, cymantrene, $(C_5H_5)Mn(CO)_3$, and cobaltocene, $(C_5H_5)_2Co$. To control a relevant variable involved in this attenuation a pulse sequence has been devised to progressively reduce the dipolar dynamics. Since it reduces the evolution of the polarization echo it is referred as REPE sequence. Two extreme behaviors were found while characterizing the materials: In systems with a strong source of relaxation and slow dynamics, the attenuation follows an exponential law (cymantrene). In systems with a strong dipolar dynamics the attenuation is mainly Gaussian. By the application of the REPE sequence the characteristic time of the Gaussian decay is increased until the presence of an underlying dissipative mechanism is revealed (cobaltocene). For ferrocene, however, the attenuation remains Gaussian within the experimental time scale. These two behaviors suggest that the many body quantum dynamics presents an extreme intrinsic instability which, in the presence of small perturbations, leads to the onset of irreversibility. This experimental conclusion is consistent with the tendencies displayed by the numerical solutions of model systems.

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I. INTRODUCTION

Nuclear spin dynamics, often called spin diffusion, is a powerful tool [1] to analyze both the local and long range structure in solids. Since the spin diffusion rate depends on the internuclear dipolar interactions, it contains useful information on the spatial proximity of the nuclei and on the dimensionality of the interaction network [2]. Therefore, there is a great interest in new pulse sequences applicable to a broad range of systems. This is the case of the pulse sequence devised by S. Zhang, B. H. Meier, and R. R. Ernst [3] (ZME) which creates a *local* polarization (LP) in a homonuclear spin system (*I*-spins) and detects its later evolution. A central point of this sequence is that it uses the presence of rare *S*-spins to label each of the *I*-spins directly bonded to them. Therefore, no spectral resolution of *I*-spins is required. This sequence has been successfully applied to several systems with different purposes [4–7] and, recently, it has been generalized [8] to be used under magic angle spinning (MAS) increasing its potential applications. On the other hand, it allows one to monitor the formation of a *polarization echo* (PE) [3] when, by external means, the LP evolution is reversed. This is achieved by a change of the sign of the effective dipolar Hamiltonian [9]. The initial localized polarization evolves into multiple-spin order during a time t_R and then, suitable pulses switch $\mathcal{H} \rightarrow -[2]\mathcal{H}$, retracing the dynamics and building up a PE at $t \approx t_R + [\frac{1}{2}]t_R$.

Despite the fact that the dominant part of the Hamil-

tonian is reversed, the PE amplitude (M_{PE}) attenuates as the time t_R grows. The study of this attenuation might provide a new characterization tool which so far has not been exploited. Furthermore, it should be possible to use the PE attenuation to obtain additional information on the underlying stochastic processes that destroy the dipolar spin coherence and inhibit the echo formation. Such procedure resembles the use of the Hahn’s echoes [10] to detect molecular diffusion [11]. In this sense, there is an obvious interest in experimental approaches allowing a proper characterization of this attenuation for different dipolar coupled systems. While a dependence of M_{PE} on time and the spinning rate has been already reported [8], there is still a need to extend these studies to different systems. As a first step to use the PE attenuation as a practical tool, we should investigate its functional dependence on t_R and, if possible, identify its physical origin. In principle, there could be many possible mechanisms contributing to the attenuation of the PE. A non-exhaustive list includes: non inverted terms in the Hamiltonian, pulse imperfections, local relaxation, spin motion, etc. Our idea involves the use of a set of systems where most of these variables remain essentially unchanged. Within the metallocenes family we can find compounds which allow us to change the dipolar interaction network and independently the magnetic nature of the metallic nuclei, this is, we can change the strength of a local source of relaxation. This would allow us to analyze whether the dipolar interaction plays any role

in the attenuation and how the presence of irreversible processes manifests in the decay rate.

In this work, we used the ZME sequence to study the PE attenuation in a set of polycrystalline samples. In all these systems, the molecular structure contains one or two cyclopentadienyl rings where only one ^1H -spin is labeled by the rare ^{13}C -spin. Our results confirm, as it was suggested by recent experiments [7], that there are systems where the decay is exponential while there are others where it is Gaussian. However, a combination of both behaviors is observed in a third class of systems. In order to understand this and, at the same time, to test the role of the dipolar interaction, we devised an *ad hoc* multiple pulse sequence, based on the ZME one, to progressively slow down the dipolar dynamics while the non-invertible interactions are kept constant.

While other mechanisms cannot be completely ruled out, our experimental results are consistent with the hypothesis that the dipolar dynamics controls the attenuation. In some samples, if the dynamics is sufficiently reduced, a crossover from the Gaussian to the exponential attenuation law can be observed. We present exact numerical solutions of the spin dynamics in a cyclopentadienyl ring and in a double ring molecule, which give further support to our hypothesis. They illustrate how the spin dynamics, in the presence of either small residual interactions or strong relaxation processes, increases the PE attenuation.

II. EXPERIMENTAL METHODS

We analyzed the PE attenuation in polycrystalline samples of ferrocene [12], $(\text{C}_5\text{H}_5)_2\text{Fe}$, cymantrene [13], $(\text{C}_5\text{H}_5)\text{Mn}(\text{CO})_3$, and cobaltocene [14], $(\text{C}_5\text{H}_5)_2\text{Co}$ and in a single crystal sample of ferrocene, all with natural ^{13}C isotopic abundance. At room temperature, these compounds crystallize in a monoclinic form with space group $P2_1/a$. The cyclopentadienyl rings perform fast rotations around their five-fold symmetry axis leading to inhomogeneous ^{13}C spectra, where the resonance frequency depends on the angle between the external magnetic field and the molecular symmetry axis. All the NMR measurements were performed in a Bruker MSL-300 spectrometer, equipped with a standard Bruker CP-MAS probe.

The ZME sequence to reverse the LP evolution is schematized in Fig. 1a. As we mentioned above, the central idea is to use the rare ^{13}C spin (S -spin) as a *local* probe to inject magnetization to one of the abundant ^1H -spins (I -spins) and to capture what is left after the I -spins have evolved. In the first part, the S -spin is polarized by means of a Hartmann-Hahn cross polarization [15] (CP). After that, the S polarization is kept spin-locked for a time t_S while the remaining proton coherence decays to zero. Then, **A**) A short CP pulse of duration t_d selectively repolarize the I_1 -spin directly bonded to the

S -spin, creating the initial localized state (t_d is the time when the first maximum in a simple cross polarization transfer occurs [16]); **B**) The LP evolves during a time t_1 in the rotating frame under a strong spin-lock field with the effective Hamiltonian

$$\mathcal{H}^y = \left[-\frac{1}{2} \right] \sum_{j>k} \sum_k d_{jk} \left[2I_j^y I_k^y - \frac{1}{2} (I_j^+ I_k^- + I_j^- I_k^+) \right]. \quad (1)$$

The interaction parameters

$$d_{jk} = -\frac{\mu_0 \gamma_I^2 \hbar^2}{4\pi r_{jk}^3} \frac{1}{2} \langle 3 \cos^2 \theta_{jk} - 1 \rangle, \quad (2)$$

are time averaged due to the fast rotation of the rings. Here, γ_I is the gyromagnetic factor of the I -spin, the r_{jk} 's are their internuclear distances and θ_{jk} are the angles between internuclear vectors and the static magnetic field. **C**) A $(\pi/2)_x$ pulse tilts the polarization to the laboratory frame where the I -spins evolve with $-[2] \mathcal{H}^z$ during a time t_2 . A $(\pi/2)_{-x}$ pulse leads the polarization back to the rotating frame. During t_2 , the effective Hamiltonian $-[2] \mathcal{H}^y$, produces the refocusing that builds up the PE at $t_2 \approx [\frac{1}{2}] (t_1 + t_d) = [\frac{1}{2}] t_R$ [6]. **D**) A short CP pulse transfers the polarization back to S . **E**) The S polarization is detected while the protons are kept irradiated. The PE attenuation can be monitored as a function of t_R by setting different values for t_1 . As discussed below, a sequence where the evolution in the laboratory frame precedes the refocusing in the rotating frame (Fig. 1b) is more appropriate to compare attenuations in different systems.

In order to test the effect of the dipolar dynamics in the PE attenuation, we replace the **B**) and **C**) parts of the ZME sequence by n defocusing and refocusing periods of $t_1 = t_R/n$ and $t_2 = [\frac{1}{2}] t_1$ respectively. Therefore, the transfer of single-spin order into multiple-spin order, for a given time t_R , can be gradually reduced by increasing n . Hereafter we will refer to this as the Reduced Evolution Polarization Echo (REPE) sequence. It includes extra refocusing periods $t_m/2 \approx [\frac{1}{2}] t_d/2$ to compensate the proton spin evolution during the CP periods. This allows us to have an experimental point to properly normalize the data. The resulting multiple pulse sequence is shown in Fig. 1c. For $n = 1$ the REPE sequence differs from the ZME one by the extra periods $t_m/2$. From a practical point of view, it is important to adjust the relative phase and the RF amplitude of the $X, -X, Y, -Y$ channels [17] since small errors produce a significant signal loss.

III. RESULTS AND DISCUSSION

As a first step, we measured the PE amplitude as a function of t_R for all polycrystalline samples. The normalized experimental data are shown in Fig. 2. These

experimental data correspond to molecules with their symmetry axes approximately perpendicular to the external magnetic field (they were frequency selected from the ^{13}C spectrum). We used the ZME sequence with $\omega_{1I}/2\pi = 44.6$ kHz, $t_C = 2$ ms, $t_S = 1$ ms, $t_d = 85$ μs , for ferrocene and $t_d = 95$ μs , for cymantrene. In the case of cobaltocene, the short relaxation time $T_{1\rho}^S \approx 780$ μs causes a significant ^{13}C signal loss if long CP or spin lock periods are used. Therefore, we maximized the first polarization transfer by setting $t_C = t_d = 85$ μs and we chose $t_S = 150$ μs which is long enough to allow for the loss of proton spin coherence and short enough to prevent a considerable signal loss.

Clearly, the three samples show a different functional dependence of the decay of the PE on t_R . In the cymantrene sample the decay is clearly exponential while in ferrocene it is Gaussian. The decay for cobaltocene is more complex. Its fitting was possible only after the implementation of the pulse sequence of Fig. 1c as explained below. It contains both exponential and Gaussian contributions. Taking into account that in ferrocene the intermolecular I - I interactions are very important while in cymantrene the rings stay relatively isolated within the experimental time scale, we set asymptotic values of 0 and 0.2 respectively. Thus, the solid lines are fittings with the characteristic time as the only free parameter. In the case of cobaltocene there are two characteristic times.

The exponential decay can be considered as a manifestation of the presence of a strong irreversible process characterized by a time τ_ϕ . According to the Fermi Golden rule, the exponential decay is the signature of a weak interaction with each of the states in a wide band of a continuous spectrum [18]. The interaction with each degree of freedom is weak but the overall effect results in a strong irreversible process. What interactions are present in cymantrene and cobaltocene but not in ferrocene? In the cymantrene sample, the strong local relaxation could be due to the quadrupolar nature of the Mn nucleus in a low symmetry environment while in cobaltocene it is more probably due to the paramagnetic nature of the Co(II).

The sources of Gaussian decay in ferrocene and the Gaussian factor in cobaltocene are less obvious. When we take into account the magnitude of the intermolecular dipolar interaction in these compounds, we observe that it grows from cymantrene to cobaltocene. Then it is important to evaluate if the magnitude of the dipolar interaction relative to \hbar/τ_ϕ is playing any role in determining the type of decay.

It should be mentioned a subtle issue underlying the comparison of the attenuations in different systems. Since there is some I -spin evolution during the cross polarization time, we do not have an experimental value for M_{PE} at $t_R = 0$. Hence, the normalization of the signals depends on the functional decay chosen in the fit-

tings. While in ferrocene and cymantrene systems this was not particularly demanding because of the obvious simple functional dependences they presented, this can be a serious restriction in a more general situation. In such a case, the pulse sequence sketched in Fig. 1b should be used. Here, the amplitude at the maximum $M_{PE}(t_2 = t_m; t_1 = 0)$ constitutes an experimental reference to normalize regardless of the functional law of the decay. The other way to overcome this problem is to employ the REPE sequence sketched in Fig. 1c and described in the experimental section. This has the additional advantage of controlling the complexity reached by the dipolar order.

We applied the REPE sequence to a ferrocene single crystal. Fig. 3 shows the ^{13}C -NMR spectrum (with the sequence parameters given in the caption). Each peak corresponds to one of the two magnetically inequivalent sites in the crystal. The carrier frequency was finely tuned to correspond to one of them. The good signal to noise ratio allows us to detect small fractions of the initial polarization. The attenuation of the PE for $n = 1$ is shown in Fig. 4. The well-defined Gaussian decay confirms the results obtained for the polycrystalline sample. The compensating periods $t_m/2$ allow us to properly normalize the data at $t_R = 0$. Besides, the unbounded nature of the spin network justify an asymptotic value of 0 for M_{PE} . The solid line represents a fitting with $M_{PE}(t_R) = \exp(-\frac{1}{2}(t_R/\tau_{mb}^1)^2)$, obtaining $\tau_{mb}^1 = (245 \pm 5)$ μs . When we set $n = 2, 8, 16$ (inset Fig. 4), the Gaussian decay is kept but its characteristic time τ_{mb}^n grows. As we discuss below, this is in agreement with our hypothesis that the time scale for the Gaussian attenuation is controlled by the dipolar interaction itself. We found that τ_{mb}^n grows as $\tau_{mb}^n = a \cdot n + b$ with $a = (54 \pm 2)$ μs and $b = (210 \pm 10)$ μs .

When applying the same sequence to the cobaltocene sample we observe a rather different behavior. While the dipolar interaction network is quite similar to the ferrocene one, the paramagnetic Co(II) atom introduces a strong source of relaxation. Thus, we expect a dipolar dynamics similar to that of ferrocene but convoluted with an extra relaxation mechanism. Fig. 5 shows the PE attenuation in the cobaltocene sample as a function of t_R for $n = 1, 2, 5, 8, 16$. There is a clear crossover from a Gaussian decay to an exponential one. This is the main result of this paper. The solid lines are fittings of the experimental data to the equation

$$M_{PE}(t_R) = \exp \left[-t_R/\tau_\phi - \frac{1}{2} (t_R/\tau_{mb}^n)^2 \right]. \quad (3)$$

Based on the results for ferrocene we set a linear dependence of τ_{mb}^n on n . This leaves only three free parameters for the whole data set. By increasing n , M_{PE} reaches an asymptotic exponential decay with $\tau_\phi = (640 \pm 20)$ μs . This shows that the Gaussian factor can be gradually reduced until the underlying exponential decay becomes

dominant. Once this regime is reached, further increment of n does not produce any effect. Expression (3) must be considered as an empirical one to account for the experimental results.

At this point it is important to mention the difference between our results and those that could be expected by considering the analogies of the REPE sequence with the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence [11] used to identify the contributions that attenuate the Hahn echo. If a single echo pulse sequence is applied, the amplitude of the Hahn echo at time t_H is proportional to $\exp[-t_H/T_2 - (t_H/\tau_D)^3]$. Here T_2 represents some processes not inverted by the Hahn echo and τ_D the molecular diffusion process in presence of field gradients. When the single echo pulse sequence is replaced by a train of n pulses spaced apart by t_H/n , the signal at the time t_H , is proportional to

$$\left\{ \exp\left[-\frac{t_H}{n}/T_2 - \left(\frac{t_H}{n}/\tau_D\right)^3\right] \right\}^n \quad (4)$$

It is obvious that for large n this becomes a single exponential, being the diffusion term eliminated by the train of pulses. One might think that a similar argument could be used to explain why a train of pulses eliminates the Gaussian factor in (3). However, one should understand the conditions for the validity of (4) to see whether equivalent conditions apply to the REPE sequence. In order to have a contribution affected by a train of pulses, its originating process must be affected. This is independent of the particular decay law. The condition that justifies the multiplication of echo amplitudes in (4) is that at each intermediate echo the initial conditions are recovered, although with a lower amplitude. This requires that the missed amplitude must not retain any correlation, classical or quantum, with the observed state. In the case of molecular diffusion, which in principle might lead to classical correlations, these are destroyed by the π -pulse because the phase acquired from the field gradient accumulates excluding the backdiffusive events from contributing to the observed polarization. Now let us go back to the REPE sequence. On the basis of our experiment we have two categories of processes. The ones characterized by τ_ϕ are not modified by the pulse sequence and hence are not related to the variables affected by these pulses. With respect to the other, we first observe that while amplitude is modified by n it does not follow the product law. From this last point we learn that correlations classical or quantum are present. The pulse sequence is intended to modify dipolar spin dynamics. However, other effects are simultaneous: Pulse imperfections and higher order terms of the average Hamiltonian which are not inverted. A major part of the pulse imperfections is accounted for by the renormalization of the attenuation curves. While the remaining effects could, in principle, affect the PE attenuation, reasonable magnitudes included in the numerical simulations in small systems (see next section) can-

not account, by themselves, for the observed time scale of the decay. An effect present in the real experiments is the unboundedness of the spin system. This huge space becomes available to the spin correlations at a rate controlled by n . Since they are entangled with non inverted interactions, they could make it available to irreversible processes. While the experiments, standing alone, cannot rule out other phenomena, they lead us to tentatively attribute a major role to the spin dynamics in the changing part of the attenuation. In order to get an insight on how this mechanism emerges, we resort to the further hints provided by numerical calculations on model systems.

IV. NUMERICAL SOLUTIONS

The ZME sequence can only change the sign of the secular part of the homonuclear dipolar Hamiltonian. Then, all the non-secular interactions are uncontrolled processes that contribute to the attenuation of the PE. Here, we will consider their effects calculating the exact evolution of the LP during the defocusing and refocusing periods in a cyclopentadienyl ring and in a complete molecule of ferrocene with a single ^{13}C .

Let us consider that the initial state, with only the I_1 spin polarized, evolves during a time t_R with the Hamiltonian

$$\mathcal{H}^1 = \mathcal{H}^y + \mathcal{H}_I + \mathcal{H}_{n.s.}^y + \mathcal{H}_{IS} = \mathcal{H}^y + \Sigma, \quad (5)$$

where

$$\mathcal{H}_I = -\hbar\gamma_I B_{1I}^y \sum_k I_k^y \quad (6)$$

and

$$\mathcal{H}_{IS} = \sum_k b_k 2I_k^z S^z. \quad (7)$$

Here, \mathcal{H}^y (described by Eq. (1)) and $\mathcal{H}_{n.s.}^y$ are the secular and non-secular parts of the I -spin dipolar interaction respectively. \mathcal{H}_{IS} is the non-secular heteronuclear dipolar Hamiltonian. Taking into account ideal $(\pi/2)$ pulses the evolution continues for a time $t_R/2$ with $-[2]\mathcal{H}^y$. We explicitly neglect the heteronuclear interactions during this period, since it was verified that they do not produce any visible attenuation in the observed time scale. In this way, the S -spin appears only in (7), and its effect can be taken into account by replacing $\mathcal{H}_{IS} \rightarrow \sum_k b_k I_k^z$. This substitution reduces to one half the computations involved. Figure 6 shows the PE amplitude as a function of t_R . The Gaussian fitting of the ferrocene experimental data (Fig. 4) is included for comparison. Even when these numerical results cannot reproduce the experimental data, they show that the non inverted interactions produce a considerable destruction of the dipolar coherence which manifests in the decay of M_{PE} . The dipolar

coupling with the ^{13}C spin is the most relevant term to produce attenuation in the presence of spin dynamics, although in its absence, it does not produce a significant decay, as it is shown by the oscillating curve in Fig. 6 where a single proton is present. The calculations for a ring of five dipolar coupled protons and for two rings show that the attenuation increases as more spins are included. This trend implies that, in the highly connected actual interaction network, a stronger attenuation, approaching the experimental curve, should be expected. Conversely, the sequence of solutions going up in Fig. 6, can be associated to a progressive reduction of the dynamics obtained through the application of the REPE sequence. In analogy with the inset in Fig. 4, it would reach the absence of decay when dynamics is totally hindered ($n \rightarrow \infty$). The lesson to be drawn from this calculation is that a small non inverted term, although non relaxing by itself, if mounted on a complex spin dynamics, it is amplified and leads to strong dynamical irreversibility. Thus any reduction of the complexity of the dipolar order (increase of n in our experiment) will decrease the amplification effect. While this slows down the polarization echo decay, an asymptotic time scale is not reached. This is the case of the ferrocene system.

Another kind of uncontrolled processes that could contribute to the PE attenuation are those producing an exponential irreversibility. As a model for these we can consider a fluctuating isotropic magnetic field. For simplicity, we assume it is only effective during the evolution in the rotating frame. Thus, the evolution of the density matrix during t_R is given by the quantum master equation [1]:

$$\begin{aligned} \frac{d\rho}{dt} &= -\frac{i}{\hbar} [\mathcal{H}^1, \rho] - \frac{1}{2\tau_\phi} \sum_{\alpha=x,y,z} \sum_j [I_j^\alpha, [I_j^\alpha, \rho - \rho(\infty)]] \\ &= -\frac{i}{\hbar} [\mathcal{H}^1, \rho] - \widehat{\Sigma}(\rho - \rho(\infty)). \end{aligned} \quad (8)$$

Notice that in the absence of dynamics ($\mathcal{H}^y \equiv 0$) we would obtain $\langle I_1^y \rangle \simeq \exp(-t_R/\tau_\phi)$. As in the previous calculation, the period of refocusing is governed by the Hamiltonian $-[2]\mathcal{H}^y$. Fig. 7 shows the results for a single cyclopentadienyl ring. Initially the decay follows an exponential law with a characteristic time τ_ϕ . However, after a while, it switches to an exponential with a shorter characteristic time. The typical time for this change is controlled by the dipolar dynamics. This can be clearly seen by considering different time scales (\hbar/d) for the dipolar interaction (Fig. 7). However, in our small systems, the decay rate of the new exponential is not affected by this dynamics. Simulations on systems with different sizes show that this rate increases with the number of spins involved in the dynamics. Hence, we can expect that in unbounded systems, where the number of correlated spins increases progressively, the decay could not be represented by any finite number of switches. In that sense,

when the dipolar dynamics is strong as compared with the exponential process ($\tau_{mb} < \tau_\phi$), the observed Gaussian tail can be thought of as a continuous switch between progressively stronger exponential decays. In the reciprocal case ($\tau_\phi < \tau_{mb}$), the experimentally relevant decay occurs while the exponential process is dominant.

The lesson learned from these numerical results, is that there is an emergent phenomenon in large many body systems through which spin dynamics favors the irreversible processes. This phenomenon is the quantum analogous to the one observed in a classical gas of rigid disks [19]. The many body interaction creates an instability that amplifies the numerical rounding errors progressively limiting the efficiency of the time reversal. Similarly, for a local spin excitation in a lattice, evolving according with a cellular automaton dynamics [20], a single spin flip (not included in this dynamics) prevents the full reversal of the polarization to the original site producing its spreading.

V. CONCLUSIONS

We have studied the decay of the polarization echoes in different systems. The ZME sequence in its original version, or even better in its modified version providing a proper normalization, allows one to distinguish between a tentative classification which recognizes two kinds of systems. They are the dipolar dominated ones, which present a Gaussian component that can be reduced by the REPE sequence (like ferrocene and cobaltocene), and those with strong sources of relaxation where an exponential decay is already manifested with the ZME sequence (cymantrene).

The REPE sequence, designed to reduce the time scale of the spin dynamics by increasing the number n of pulses, is able to give further information on the first group by revealing the existence of underlying relaxation mechanisms for large enough n 's as it is the case of cobaltocene. Looking for an experimental test to rule out possible experimental artifacts in these results, one could resort to alternative pulse sequences which also achieve the dynamics reversal with less demanding train pulses [21,22]. Further tests of the sensitivity of the REPE sequence as a tool to characterize new materials are experiments in which a dipolar dominated system is progressively doped with local centers of relaxation (e.g. a solid solution of cobaltocene in ferrocene). Besides, the REPE sequence can be readily adapted to be used under MAS by rotor synchronizing the pulses according to the prescriptions of ref. [8].

Because of the deep physical meaning of the Polarization Echo, beyond its potential applications as a practical tool, the ZME and REPE sequences open an exciting new field of study in fundamental physics. It is the

onset of irreversibility in interacting many body quantum systems. This is a particular area of the growing discipline of quantum chaos [23] whose theoretical development is still in its infancy. On one side the magnitude of the polarization echo coincides with the most convincing signature of quantum chaos [24]: the exponentially fast decrease of the overlap between states evolved, from the same initial condition with slightly different Hamiltonians \mathcal{H} and $\mathcal{H} + \Sigma$. The connection is evident for a system of N interacting spins since we can write $M_{PE} = 2^N \text{Tr}(\rho_{\mathcal{H}}\rho_{\mathcal{H}+\Sigma}) - 1$, which is a way to evaluate this overlap. This expression has close resemblance to some definitions of entropy [25]. Independently, $-\ln[M_{PE}(t_R)]$ is a measure of how the inefficiency in our dynamics reversal increases with time. When the polarization is a conserved magnitude within the observed time scale, $M_{PE}(t_R)$ is a measure of the inverse of the volume Ω_{t_R} occupied by the polarization at the PE time: $-\ln[M_{PE}(t_R)] \propto \ln[\Omega_{t_R}]$ which gives an “entropic” meaning for both the overlap and the polarization echo. To further visualize this, one might assume that after a few pulses the shape of the distribution function for the refocused polarization (e.g. $P(x, t) = 1/\Omega_t$ for $|x| < \Omega_t/2$ where t is an echo time) remains the same (i.e. the echo would represent a scale transformation). In this case $-\int P(x) \ln[P(x)] dx$ grows proportionally to $-\ln[P(0, t_R)] = -\ln[M_{PE}(t_R)]$.

Thus, the Gaussian regime for the attenuation of the PE in our experiments seems to indicate an anomalous decrease (growth) of the overlap (“entropy”) not predicted within any of the present one body theories. Our experiments might be interpreted as an indication that *infinite* interacting many body quantum systems present an extreme intrinsic instability towards dynamical irreversibility. The experiments, even with imperfections, are much ahead of the possibilities of the current theory and they have the leading word.

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Figure 1: **a)** ZME sequence for refocusing the dipolar evolution of the ^1H spin polarization in the laboratory frame (see text). The solid and dashed lines show the main and secondary amplitude polarization pathways **b)** Alternative version of the ZME sequence where the refocusing occurs in the rotating frame. The polarization maximum at $t_2 = t_m$ provides an experimental point for data normalization. It allows a straightforward comparison of the PE attenuation in different systems. **c)** Reduced Evolution Polarization Echo (REPE) sequence to control the dipolar spin dynamics. For a given time t_R , setting $t_1 = t_R/n$ and $t_2 = [\frac{1}{2}] t_1$, the development of multiple spin order is reduced by increasing n .

Figure 2: Normalized polarization echo amplitude as a function of t_R for polycrystalline samples of cymantrene, ferrocene and cobaltocene, using the ZME sequence. The lines are fittings to a Gaussian (ferrocene), exponential (cymantrene) and a product of both functions (cobaltocene).

Figure 3: ^{13}C NMR spectrum of a ferrocene single crystal using the REPE sequence with: $n = 1$, $\omega_{1I}/2\pi = 62$ kHz, $t_C = 2$ ms, $t_S = 1$ ms, $t_d = 53$ μs and $t_R = 8$ μs . The two peaks indicate the presence of two magnetically non-equivalent sites. The on resonance peak corresponds to molecules with its fivefold molecular symmetry axis at approximately 20° with respect to the external magnetic field.

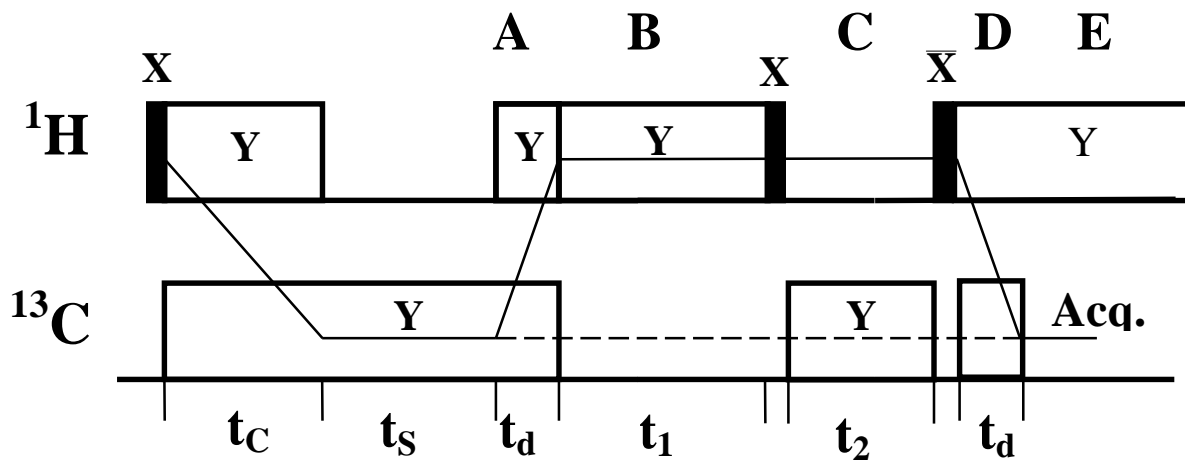
Figure 4: Attenuation of the polarization echo in the ferrocene single crystal as a function of t_R for $n = 1$ (REPE sequence). The line represents a Gaussian fitting with the characteristic time $\tau_{mb}^1 = (245 \pm 5)$ μs as the only free parameter. **Inset:** PE attenuation for progressively reduced dipolar dynamics, $n = 1, 2, 8, 16$. No asymptotic regime is reached within the experimental time scale. The solid lines are Gaussian fittings yielding characteristic times $\tau_{mb}^2 = (335 \pm 10)$ μs , $\tau_{mb}^8 = (650 \pm 20)$ μs and $\tau_{mb}^{16} = (1070 \pm 60)$ μs .

Figure 5: Attenuation of the polarization echo in the cobaltocene sample as a function of t_R for $n = 1, 2, 5, 8, 16$ with $\omega_{1I}/2\pi = 56$ kHz, $t_C = 85$ μs , $t_S = 150$ μs , and $t_d = 85$ μs . The experimental data show a clear crossover between a dominant Gaussian attenuation to an exponential one. The solid lines represent fittings of the whole set of data to equation (3) yielding $a = (130 \pm 10)$ μs , $b = (90 \pm 10)$ μs and $\tau_\phi = (640 \pm 20)$ μs .

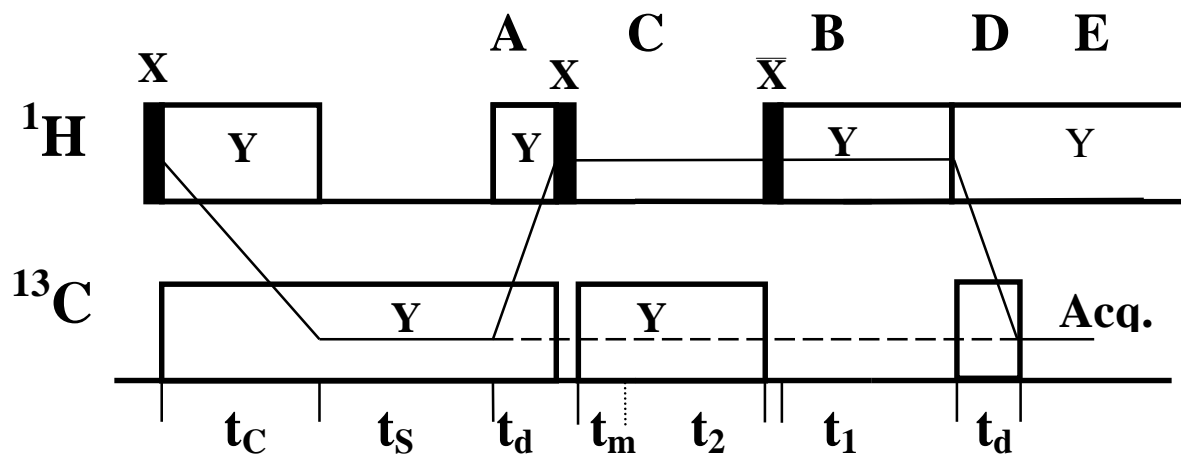
Figure 6: Numerical calculation of the attenuation of the polarization echoes considering the effects of the non-inverted interactions. The thick solid and dashed lines correspond to a cyclopentadienyl ring and to a ferrocene molecule respectively. The Gaussian curve is the fitting of the ferrocene experimental data of Fig. 4. The attenuation is mainly caused by the destruction of the dipolar coherence induced by the heteronuclear dipolar coupling. \mathcal{H}_{IS} does not produce relaxation in the absence of homonuclear dipolar interactions (oscillating curve).

Figure 7: Attenuation of the polarization echoes for a cyclopentadienyl ring considering an exponential irreversible process (See Eq. (8)). The different curves represent a progressive expansion of the dipolar time scale (\hbar/d). Here $d_1 = 2610$ Hz $\times 2\pi\hbar$ is the nearest neighbor dipolar coupling. The initial decay rate, $1/\tau_\phi = 500$ Hz, switch to a stronger one after a while. The upper curve correspond to the exponential decay, $\exp(-t_R/\tau_\phi)$, in the absence of dipolar dynamics.

a)



b)



c)

